

Thermal Plasma Synthesis of SiC-Si_3N_4 Composite Powders from $SiCH_3Cl_3$-NH_3-H_2

H.-S. Seon and S.-W. Rhee

SiC-Si_3N_4 composite powders were synthesized by introducing trichloromethylsilane, ammonia, and hydrogen into a high-temperature radiofrequency (RF) thermal plasma argon gas. Powders were characterized by XRD, TEM, and FT-IR. Silicon carbide and silicon nitride were formed independently into separate powders. Silicon carbide was formed as β-SiC crystalline powder and silicon nitride was in an amorphous state. The crystalline SiC powders were in the size range of 75 to 200 nm and amorphous Si_3N_4 powders were 5 to 60 nm. When the mole ratio of ammonia to trichloromethylsilane was between 1 and 2, SiC-Si_3N_4 composite powders were formed, and when it was higher than 4, Si_3N_4 powders were formed.

Keywords:
composite powders, SiC-Si_3N_4 composites, thermal plasma systhesis

1. Introduction

SILICON carbide and silicon nitride are two of the most promising high-temperature structural materials and have been produced commercially from silica. Composites of SiC and Si_3N_4 have attracted much attention for their improved high-temperature strength and thermal shock resistance.[1]

SiC-Si_3N_4 composites can be prepared by simply mixing powders of each component, but the synthesis of composite powders can possibly provide a finer and more uniform mixture of SiC and Si_3N_4 phases. Gas phase synthesis of ceramic materials has attracted much attention, because it is easier to produce ultrafine and high-purity ceramic powders. One problem is that most of the gas phase reactions needed for the production of ceramic powders must be conducted at high temperatures because their equilibrium constants are usually low.

Thermal plasma synthesis is suitable for this purpose, because much higher temperatures can be obtained compared to other conventional methods. SiC-Si_3N_4 composite powders were synthesized by Fukushige *et al.* from SiO_2-N_2-H_2 through gas-solid chemical reactions at 1450 to 1550 °C.[2] Later Hojo and Kato prepared composite amorphous powder from a $Si(CH_3)_4$-NH_3-H_2 system at 1200 °C and later crystallized it into SiC and Si_3N_4 phases by heat treatment at 1550 °C.[3] In this case, it was reported that the crystallized powder had a composite structure consisting of a Si_3N_4 core and a SiC shell or a reversed structure in a single particle. They later synthesized SiC-Si_3N_4 composite powders in a DC plasma reactor from a $SiCH_3Cl_3$-NH_3-H_2 system and suggested that the composite particles had a homogeneous structure in which both Si_3N_4 and SiC phases were uniformly distributed within a particle.[4] Recently, Lee *et al.* synthesized Si_3N_4 and Si_3N_4-SiC mixed powders in a DC-RF hybrid plasma reactor from a $SiCl_4$-CH_4-H_2 system.[5] In their reactor, $SiCl_4$ was introduced upstream of the plasma and $SiCl_4$ was decomposed completely when it was carried through the plasma to form silicon molten particles. Ammonia, hydrogen, and/or methane were introduced downstream of the plasma, which nitrided and/or carburized the silicon. Pyrolysis of polyorganosilazane[6] and also laser synthesis of hexamethyldisilazane[7] were used to synthesize SiC-Si_3N_4 composite powders.

In this paper, a radiofrequency (RF) thermal plasma chemical reactor was used to synthesize SiC-Si_3N_4 composite powders from a $SiCH_3Cl_3$-NH_3-H_2 system. In this case, the Si/C

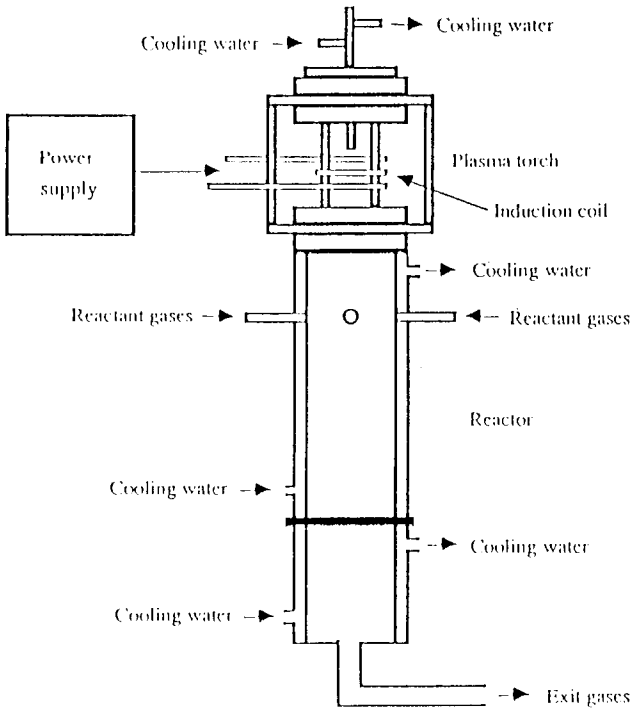

Fig. 1 Thermal plasma chemical reactor.

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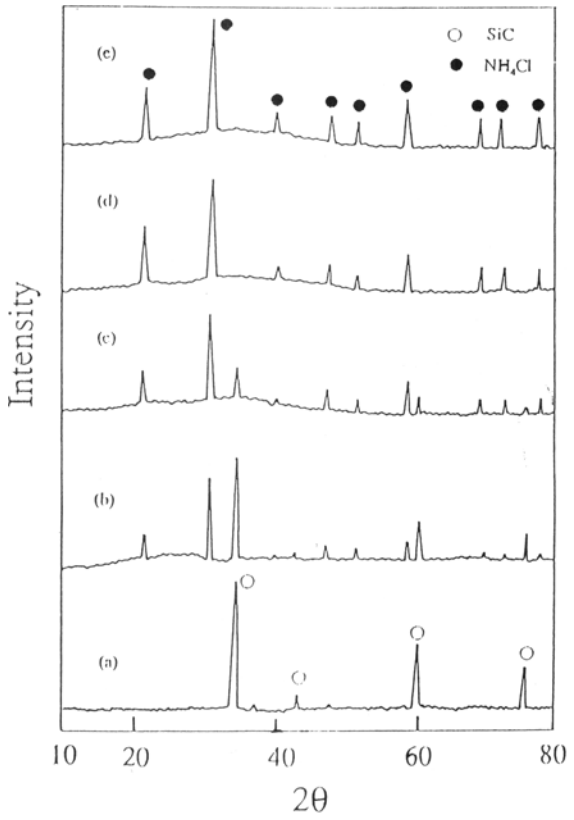

Fig. 2 X-ray diffraction patterns of powders synthesized with the mole ratios of NH_3 to $SiCH_3Cl_3$ of (a) 0, (b) 1, (c) 2, (d) 4, and (e) 8 at a hydrogen flow rate of 2 liters/min.

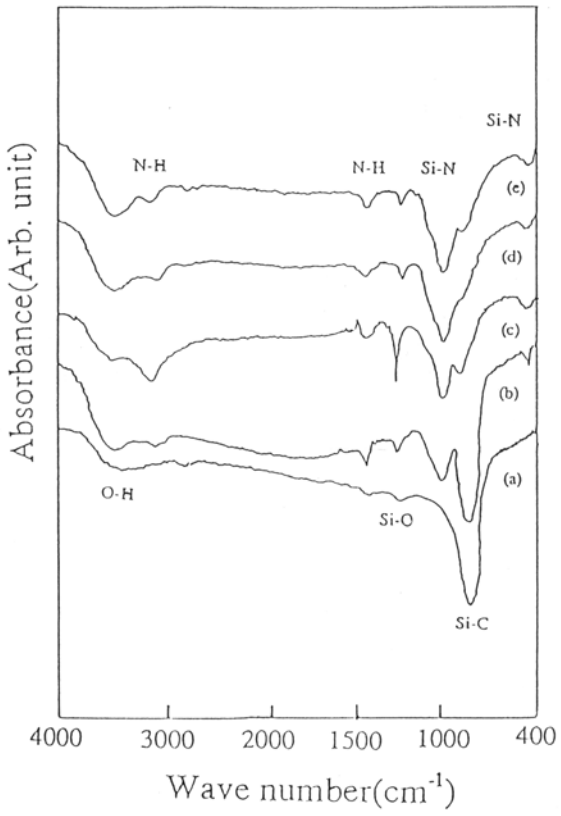

Fig. 3 Infrared spectra of powders synthesized with mole ratios of NH_3 to $SiCH_3Cl_3$ of (a) 0, (b) 1, (c) 2, (d) 4, and (e) 8 at a hydrogen flow rate of 2 liters/min.

ratio in the reactant gas mixture was fixed at 1, and the effect of the amount of ammonia introduced was studied.

2. Experiments

The RF plasma chemical reaction system used in the experiment is shown in Fig. 1. An induction coil, which wraps three turns around the double-walled and water-cooled quartz tube was connected to a 4-MHz, 25-kw RF generator. Plasma was formed inside the quartz tube with argon gas, which flowed through the torch at a rate of 50 liters/min. Hydrogen at a rate of 2 liters/min, $SiCH_3Cl_3$ at a rate of 1.3 grams/min, and ammonia at a rate of 0 to ~1.6 liters/min were introduced downstream of the plasma torch.

A bubbler containing trichloromethylsilane liquid was heated in a water bath, and the vapor was transported into the reactor with argon gas. The mole ratio of ammonia to trichloromethylsilane was varied at 0, 1, 2, 4, and 8. The reaction chamber connected to the plasma torch was 15 cm in diameter and 1 m high. Reactant gases were injected at the tail of the plasma, mixed with the high-temperature argon gas, and allowed to flow into the reactor. Powders formed in the gas phase and were quenched as they were transported downstream of the reactor. The reaction was carried out for about an hour, and most of the powder produced was recovered from the side wall of the reactor. The shape and size of the powders, their crystallinity, and their chemical compositions were analyzed using a transmission electron microscope (TEM), X-ray diffractometer (XRD), and Fourier transform infrared spectroscope (FT-IR).

3. Results and Discussion

3.1 *Crystallinity*

Figure 2 shows the X-ray diffraction patterns of powders synthesized with various amounts of ammonia. When the mole ratio of ammonia and trichloromethylsilane was zero, β phase silicon carbide was formed, as shown in Fig. 2(a). It was previously confirmed that β-SiC was formed from plasma chemical reactions.[8-11] When the ammonia was introduced, ammonium chloride formed as a byproduct, as shown in Fig. 2(b) through 2(e). The intensity of the ammonium chloride peak became larger, and that of the SiC became smaller as the mole ratio of ammonia and trichloromethylsilane increased. When the mole ratio was about 4, formation of SiC was completely suppressed. In the plasma chemical reaction of $SiCH_3Cl_3$-NH_3-H_2, silicon nitride was formed in an amorphous state and was not detected in XRD analysis. It has been reported that α phase and β phase silicon nitride powders could be synthesized by plasma chemical reactions from $SiCl_4$-NH_3.[5,12]

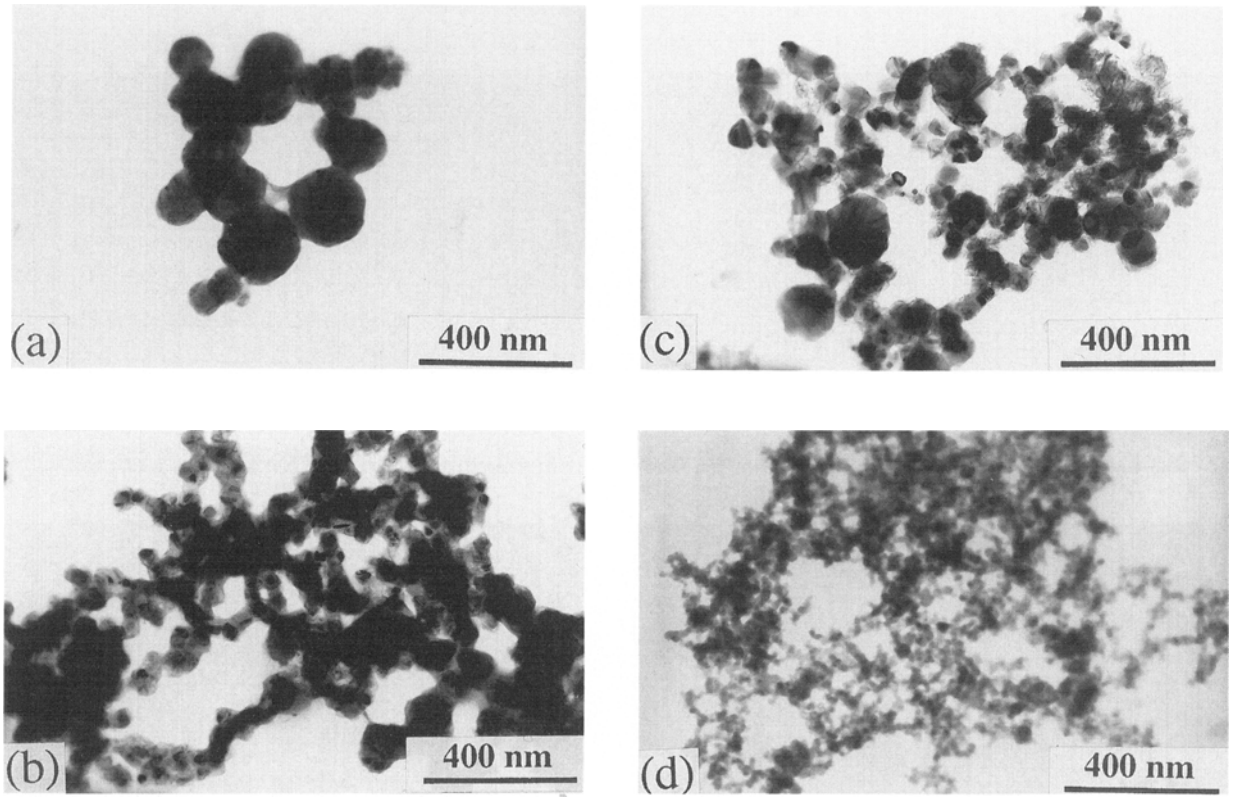

Fig. 4 Transmission electron micrographs of powders synthesized with the mole ratios of NH_3 to $SiCH_3Cl_3$ of (a) 0 (SiC powder), (b) 1 (SiC - Si_3N_4 composite powder), (c) 2 (SiC - Si_3N_4 composite powder), and (d) 8 (Si_3N_4 powder).

It has been pointed out that excess ammonia should be introduced to obtain stoichiometric silicon nitride,[5] but if the amount of ammonia was too excessive amorphous silicon nitride was formed. In our experiments, crystalline silicon nitride was not observed. When the mole ratio of ammonia to trichloromethylsilane was 4, about 60% of the powders recovered from the upper part of the reactor were ammonium chloride. The amount of ammonium chloride dropped to about 30% at the lower part of the reactor. This is probably because of the fact that the ammonia concentration decreases downstream in the reactor. This suggests that multistage injection of ammonia could reduce the formation of ammonium chloride.

3.2 *FT-IR Analysis*

FT-IR analysis was done after the ammonium chloride was removed by heating at 280 °C for 2 hours in a vacuum oven. Figure 3 shows IR spectra of powders synthesized with mole ratios of ammonia and trichloromethylsilane of 0, 1, 2, 4, and 8. When the ratio was 0, a Si-C bond appears at 800 cm^{-1}, a Si-O bond at 1200 cm^{-1}, and an O-H bond at 3400 cm^{-1}. The Si-C bond forms from silicon carbide, the Si-O bond presumably from the oxidation of the powder surfaces, and the O-H bond from the adsorption of moisture. When the ratio was 1 or 2, a Si-N bond appears at around 450 and 950 cm^{-1}. When the ratio was higher than 4 or 8, formation of the Si-C bond was not observed, as previously confirmed by XRD analysis. When the ratio was 1 or 2, Si-C and Si-N bonds appeared, as shown in Fig. 3(b) and 3(c). The peak intensity of Si-C decreased, whereas that of Si-N increased as the amount of ammonia introduced was increased. The N-H bond is probably from unremoved ammonium chloride.

In the thermal plasma synthesis of the $SiCH_3Cl_3$-NH_3-H_2 system, ammonium chloride and silicon carbide appear as crystalline powders, whereas silicon nitride appears as amorphous powders. When the ratio was zero, the product was silicon carbide, and when it was 1 and 2, silicon carbide-silicon nitride composite powders mixed with ammonium chloride were synthesized. When the ratio was more than 4, silicon nitride powders with ammonium chloride were formed.

3.3 *Transmission Electron Microscope Analysis*

Figures 4 and 5 show transmission electron micrographs and area diffraction patterns of powders synthesized at various mole ratios of ammonia and trichloromethylsilane. Figure 4(a) shows the shape of the powders synthesized at a mole ratio of zero, and Fig. 5(a) shows the diffraction pattern of these powders. β-SiC powders with regular shapes were formed. Figures 4(b) and (c) illustrate SiC-Si_3N_4 composite powders formed at mole ratios of 1 and 2, respectively. Crystalline SiC powders with relatively bigger sizes mixed with Si_3N_4 powders with relatively smaller sizes are formed. Two types of diffraction patterns were obtained for powders synthesized at the mole ra-

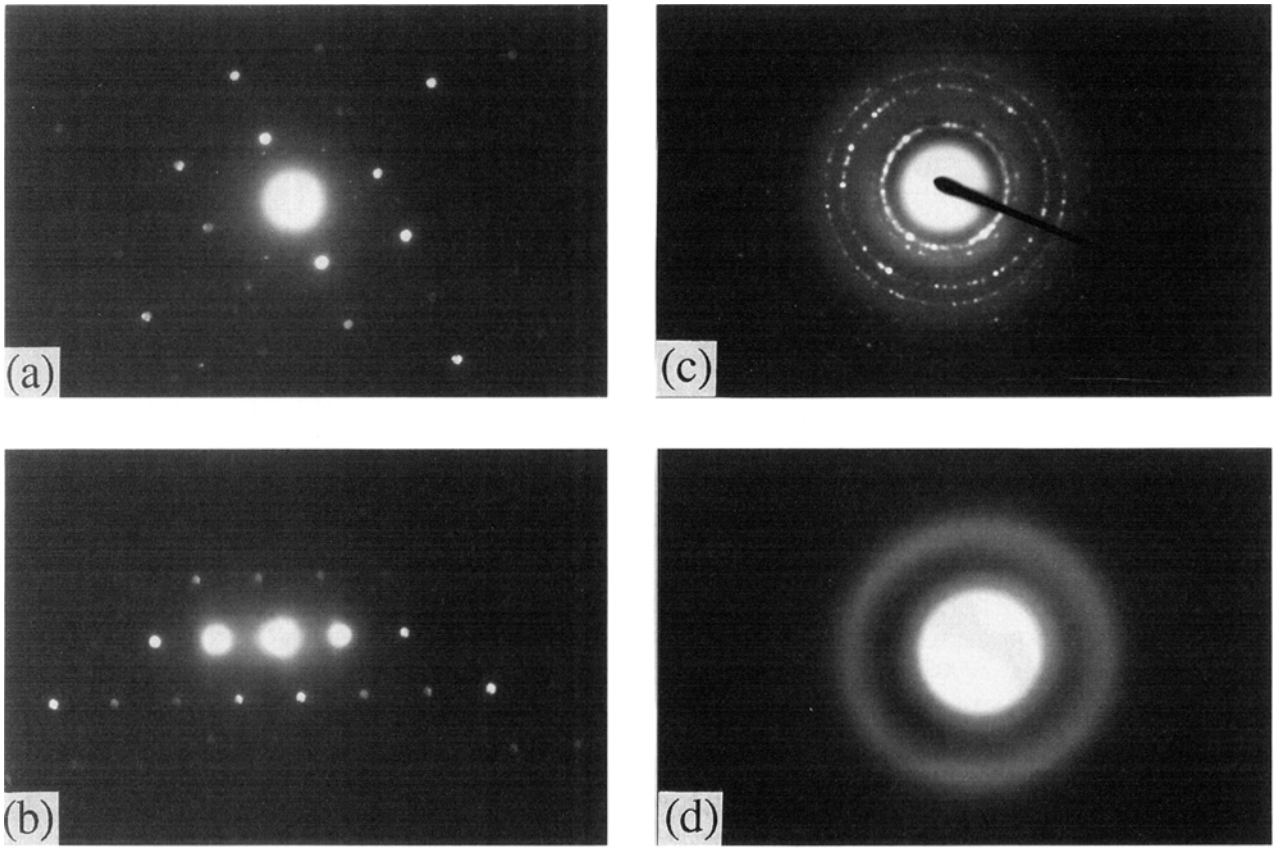

Fig. 5 Selected area diffraction patterns of powders synthesized with the mole ratio of NH_3 to $SiCH_3Cl_3$ of (a) 0 (SiC powder 013 plane), (b) 1 (SiC - Si_3N_4 composite powder, SiC 012 plane), (c) 1 (SiC - Si_3N_4 composite powder), and (d) 8 (Si_3N_4 powder).

tio of 1, as shown in Fig. 5(b) and (c) depending on the area. This confirms the existence of crystalline β-SiC powders mixed with independently formed amorphous Si_3N_4 powders. The spot pattern in Fig. 5(b) was obtained from the area where crystalline SiC powders were located, and the ring pattern in Fig. 5(c) was obtained from the area where crystalline SiC powders were mixed with amorphous Si_3N_4. Figures 4(d) and 5(d) show the transmission micrograph and diffraction pattern of powders synthesized at the mole ratio of 8. Figure 4(d) shows that most of the powders were smaller than the crystalline SiC powders shown in Fig. 4(a), and Fig. 5(d) shows that these Si_3N_4 powders are amorphous.

The size of the β-SiC powders synthesized with thermal plasma was reported to be around 70 to 200 nm.[8] Image analysis of the TEM photos also shows that the crystalline β-SiC powders synthesized in this experiment are in the same size range, but that the amorphous Si_3N_4 powders are in the size range of 5 to 55 nm.

Figure 6 shows the average particle size of the powders as a function of the mole ratio of NH_3 and $SiCH_3Cl_3$. It is clear that crystalline SiC powders grow bigger than amorphous Si_3N_4 powders in the composite mixture. As the amount of ammonia was increased, the average size of the particles became smaller. It also seems that they grow independently into separate powders and precipitate as a mixture. This is quite contradictory to the finding of Hojo and Kato that both SiC and Si_3N_4 phases were uniformly distributed in a composite particle.

3.4 *Reaction Mechanism*

The plasma flame temperature has been measured with optical emission spectroscopy by many investigators and is believed to be higher than 10,000 °C.[13] For plasma generation, a large volume of argon gas is usually used. These facts indicate that the reaction rate is very fast and that the residence time of the reactant gases in the reactor is very short. Furthermore, the reaction mechanism is usually very complicated at high temperatures. Consequently, it is nearly impossible to find out the exact mechanism of the thermal plasma chemical reactions. Because the reactant gas mixtures were introduced into the downstream portion of the plasma flame, the temperature of the reaction zone would be much lower than the plasma flame temperature.

The temperature of the reaction zone could be higher than 2000 °K, which was not confirmed in this experiment. Here, we suggest a set of qualitative reaction pathways from the experimental observations:

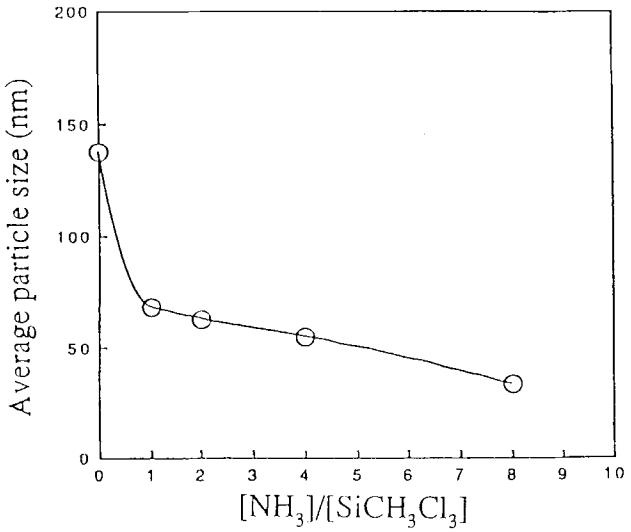

Fig. 6 Average size of powders as a function of the mole ratio of NH_3 to $SiCH_3Cl_3$ as indicated.

$$SiCH_3Cl_3\,(g) \rightarrow CH_x\,(g) + Si\,(g) + 3Cl\,(g) + (3-x)\,H\,(g) \quad [1]$$

$$H_2\,(g) \rightarrow 2H\,(g) \quad [2]$$

$$NH_3 \rightarrow NH_x\,(g) + (3-x)\,H\,(g) \quad [3]$$

$$Si\,(g) + CH_x\,(g) \rightarrow SiC\,(s) + xH\,(g) \quad [4]$$

$$3Si\,(g) + 4NH_x\,(g) \rightarrow Si_3N_4\,(s) + 4xH\,(g) \quad [5]$$

$$H\,(g) + Cl\,(g) \rightarrow HCl\,(g) \quad [6]$$

$$HCl\,(g) + NH_3\,(g) \rightarrow NH_4Cl\,(s) \quad [7]$$

$$CH_x\,(g) \rightarrow C\,(s) + xH\,(g) \quad [8]$$

$$0 \le x \le 3$$

Reactions [1] and [2], the dissociation of reactants, and Reactions [3] and [4], the formation of products, occur in the high-temperature reaction zone. Without the addition of ammonia, SiC and free carbon would be formed via Reactions [4] and [8]. If the hydrogen concentration (fugacity) is large enough, the formation of free carbon, Reaction [8], can be suppressed.[8] With the addition of ammonia, silicon nitride and ammonium chloride powders are formed via Reactions [5] and [7]. As the fugacity of ammonia is increased, the rate of Reactions [5] and [7] becomes faster. If the fugacity of ammonia is sufficiently large, carbonization, Reaction [4], can be suppressed. SiC-Si_3N_4 composite powders can be formed when there are appropriate pressures of Si(g), CH_x(g) and NH_x(g), which corresponds to the reactant mole ratio of ammonia and trichloromethylsilane, 1 and 2. Proceeding downstream of the reactor, Reaction [7] becomes less significant compared to the upstream of the reactor. This hypothesis can explain the experimental observations qualitatively.

4. Conclusion

SiC-Si_3N_4 composite powders were synthesized by plasma chemical reaction of $SiCH_3Cl_3$-NH_3-H_2. The structure and properties of the powders were studied and the following results were obtained:

1. The mole ratio of ammonia and trichloromethylsilane in the reactant gas mixture determines the amount of SiC and Si_3N_4 in the composite powders. When it was zero, β-SiC was formed, and when it was higher than 4, formation of SiC was suppressed. Between these two values, composite powders of SiC-Si_3N_4 were synthesized.
2. Composite powders consist of β-SiC and amorphous Si_3N_4, with crystalline SiC in the size range of 70 to 200 nm and with amorphous Si_3N_4, in the range of 5 to 55 nm. Crystalline SiC powders grow larger than amorphous Si_3N_4 powders.
3. SiC and Si_3N_4 grow into separate powders and precipitate as a mixture rather than uniformly distributed in a single particle.

Acknowledgment

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